

SCIENCE FOR CERAMICS PRODUCTION

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INTRODUCTION OF NANOMATERIALS AND NANOTECHNOLOGIES IN CERAMICS PLANTS

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Introduction of nanomaterials and nanotechnologies in ceramics plants has particular objective and subjective characteristics. It is expedient to begin assimilation of nanotechnologies with the use of nanopowder additives to existing ceramic pastes, especially in the form of modifying additives. Another promising method is to manufacture nanoceramics from powders of unstable solid phases in which the particle size is much larger than nanosized and nanostructures are created during heat treatment when they decompose. All stages of ceramics technology change very little here. Making nanoceramics from nanopowders is the most complicated due to the important change in the parameters of the technology. Use of negative and positive templates is promising for nanocomposites.

Key words: ceramics, nanomaterials, nanotechnologies, production.

Process engineers working in ceramics have long been familiar with nanoparticles, only they previously called them colloidal particles. The engineers knew that colloidal particles made the basic contribution to the surface of ceramic powders and are necessary for manufacturing very dense ceramics. Powders with a minimum particle size up to nanosized (< 100 nm) have been used in transparent ceramics technology. The same particles were used in fabricating a thin working layer in ceramic membranes. The size of the pores in this layer was so small that they could be used to separate molecules by size, for example, separating molecules of alcohol from molecules of water. For this reason, the gradual transition to the nanolevel began in ceramics technology approximately 40 years ago, when chemical methods became increasingly widely used to obtain highly disperse powders. We can say with justification that mastering the nanolevel is the result of the development of ceramics technology.

Let us examine the problems of introducing nanomaterials technologies in ceramics plants. Since nanotechnologies are a new level of ceramics technology, this should facilitate their introduction in ceramics plants. At the same time, the inertness of the thinking and approaches used for ceramics with an initial particle size much greater than 100 nm is caus-

ing low output of acceptable items. It is necessary to change the approaches to conducting ceramics manufacturing processes (fabrication of powders, molding pastes, molding, drying, firing). We will evaluate the prospects for manufacturing nanoceramics at ceramics plants.

With respect to the geometric parameters, ceramic nanomaterials (CNM) are divided into 0-dimensional (0D) — nanoparticles, nanoclusters, associates of defects, quantum points, and other elements of the structure smaller than 100 nm; 1-dimensional (1D) with a diameter of less than 100 nm — nanotubes, whisker crystals, nanofibers; 2-dimensional (2D), less than 100 nm thick — nanofilms, nanolayers, nanocoatings, crystal boundaries, phases, blocks; 3-dimensional (3D) — monolithic items consisting of structural elements less than 100 nm in size if the nanosized structural elements determine their most important performance property (Fig. 1). At the same time, particles of clay minerals used in production of porcelain, faience, and clay bricks have the shape of thin disks (more precisely, hexahedrons) approximately 1 nm thick. Fibers and films more than 100 nm thick are also ceramic nanomaterials if they consist of structural elements less than 100 nm in size or contain structural elements less than 100 nm in size, but only if the nanosized structural elements determine their most importance performance property.

It should be noted that structural elements with nanodimensions are always present in any traditional ceramic ma-

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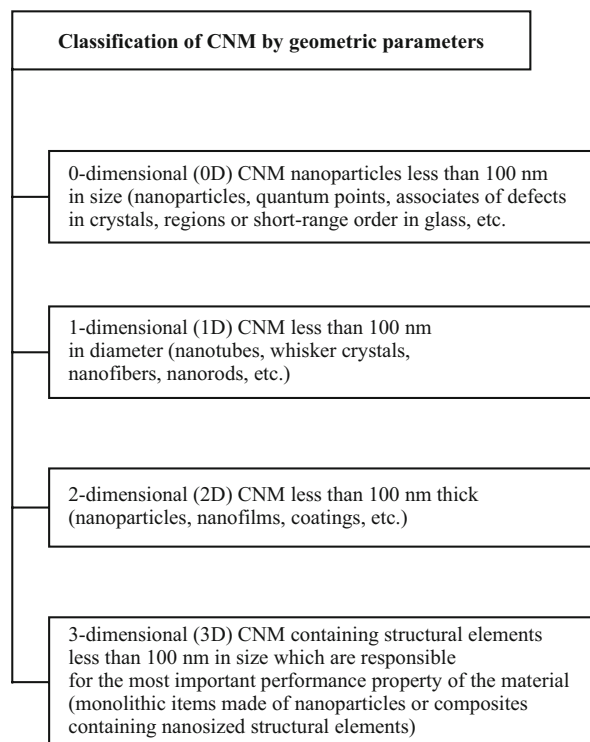


Fig. 1. Classification of ceramic nanomaterials based on geometric parameters.

terial, but they determine the most important performance property in nanomaterials. If the material (1-, 2-, 3-dimensional) not only consists of one-phase structural elements less than 100 nm in size but also contains ceramic structural elements less than 100 nm in size that determine its most important performance property, then the material can be considered a nanocomposite. Technologies for items made of nanomaterials are nanotechnologies if the processes in which the nanoparticles participate can be controlled and the presence of nanosized structural elements is responsible for their most important performance property or their use in intermediate states of the technology either makes it less expensive or produces a higher level of properties.

Ceramics in which the particle size does not exceed 100 nm can have unique properties caused by their nano-size — magnetic, electrical, etc. In these nanoceramics, the volume between nanoparticles is commensurate with the volume occupied by the particles. The boundaries have a disordered (in contrast to an ordered crystal) structure and lower density, so that the density of poreless nanoceramics is also lower than for ordinary ceramics with crystals much larger than 100 nm. These ceramics should have high plasticity (deformability) and even superplasticity (very high deformability) on heating. This opens up prospects for manufacturing ceramic items with the methods used in metallurgy — extrusion, drawing, etc. We will primarily examine 3D nanomaterials.

We know that the smaller the crystal diameter is in very dense ceramics, the higher the strength. Ceramics made of

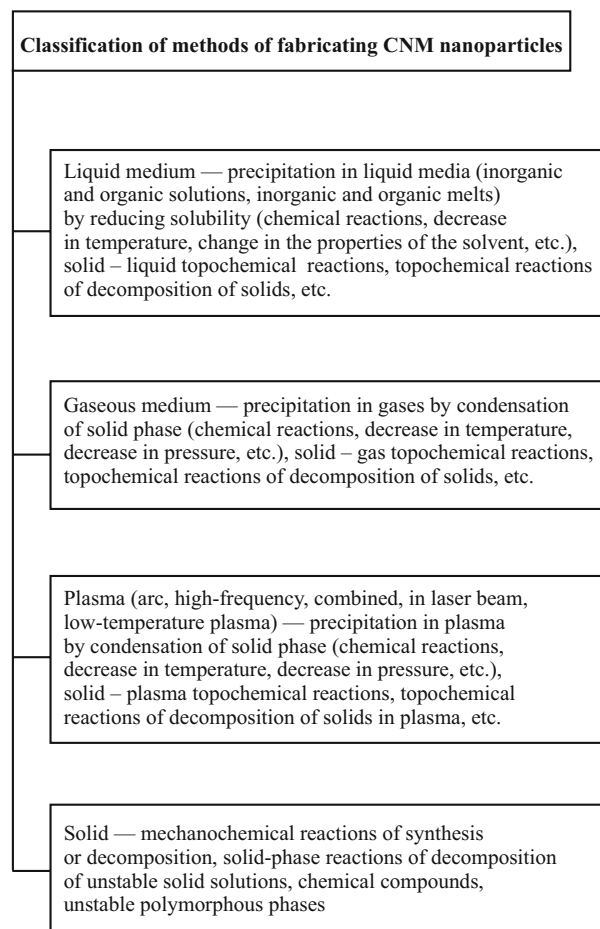


Fig. 2. Classification of methods of fabricating nanopowders by medium in which the basic formation of nanoparticles takes place.

nanocrystals should have high strength. In polishing these ceramics, extremely high surface purity can be obtained since the defects (chips) are usually comparable to the size of the crystals. However, in fabrication of such ceramics, great difficulties arise at all boundaries of the technology, especially in firing, when the material acquires strength in sintering (an increase in the strength due to sintering of contiguous particles and elimination of pores). Sintering is conducted by transfer of material from particle to particle (mass transfer) and reciprocal movement of particles (plastic deformation). The particle size usually increases, and the initial nanoparticles can easily exceed nanosized (100 nm).

The problems begin with fabricating the nanopowder, which consists of nanoparticles. The classification of methods of obtaining nanoparticles as a function of the environment where the basic process takes place is shown in Fig. 2. This division is very arbitrary, since almost all methods of obtaining nanopowders consist of several stages that take place in different media and they are all important. The medium in which the precursor is synthesized and whose treatment (usually heat treatment) results in formation of nanopowder is usually selected. Fabricating nanopowders is still

expensive, especially since they are not mass produced. Making nanopowders in-house makes sense when they are used for production of popular types of ceramics and nanocomposites or in cooperation with reliable suppliers. It is expedient to use automated lines to exclude the effect of the human factor and reliably control the process parameters, including the gaseous medium in which they take place. Many scientists believe that in view of the strong dependence of the properties of nanoparticles on their size, it is necessary to obtain powders with very similar nanoparticle sizes (monofractional).

The surface atoms have uncompensated chemical bonds directed outwards. In nanoparticles less than 10 nm in size, the proportion of surface atoms begins to exceed their content in the bulk. This is the cause of the extremely high chemical activity of nanoparticles. The high energy of the surface particles decreases the melting point in comparison to large particles. Due to the presence of uncompensated chemical bonds, nanoparticles attempt to react with the environment and join together with formation of strong aggregates. The presence of water in the gaseous medium causes aggregation, so that the powders must be stored in dry inert gases or inert organic liquids. Due to the reaction with the environment, the properties of nanoparticles can strongly change in time (aging of nanoparticles). Under the effect of the environment (temperature, pressure, chemical composition), the aggregates can be strengthened and can even grow into large crystals, which does not allow fabricating nanoceramics. Keeping the particles within the limits of nanosize dimensions is the most important problem. The same processes will take place when nanopowders are mixed with each other and with a temporary process binder. It is necessary to prevent formation of strong aggregates in the stage of fabrication of nanopowders and in fabrication of molding pastes.

A temporary process binder is added to the paste to reduce the friction between powder particles in molding semiproducts and to increase the strength of the semiproduct. The binder must cover the surface of the particles, and since it is very large in nanoparticles, the binders too must be much larger than usual. The binder is subsequently removed, and pores form where the binder was and must be removed during firing to obtain high-density ceramics. The size of the semiproduct will decrease (high shrinkage). High shrinkage not only makes it difficult to fabricate articles with precise dimensions but also creates grounds for the appearance of nonuniform densities (local compacted regions [1]) and even cracks.

Aggregation of nanoparticles will continue in the stages of molding, removal of temporary process binder, and the initial stages of sintering, which causes the appearance of denser regions (local compacted regions). This can become the cause of nonuniform crystal growth in less dense regions. This is especially manifested when water-containing binders are used, so that organic binders in organic solvents are more

promising. However, this creates problems in environmental protection and fire safety.

Due to the high chemical activity, nanoparticles can react with a polymer binder, altering its chemical composition, degree of ordering of the structure of the polymer, and in the final analysis, increasing the viscosity. This impedes uniform distribution of the binder in the molding paste and molding of equidense semiproduct or increases the binder content, which is very undesirable. Semidry compression molding, casting from slips, and less frequently, plastic molding are used for molding the semiproducts. Denser and more equidense semiproducts are obtained with methods that reduce the friction between particles (internal friction) and friction between particles and the walls of the molds (external friction): isostatic, ultrasound [2], and magnetic-pulse [3] molding. Preventing the formation of regions of local compacted regions and a dense hollow shell allows making high-density semiproducts. Semiproducts with a density of 0.7 – 0.8 of the theoretical value are thus obtained by pulsed magnetic molding. Before molding, highly disperse powders are usually granulated, and the granules should be destroyed in the concluding stage of molding, resulting in a dense and equidense semiproduct.

Casting methods are the most promising for fabricating dense and equidense semiproducts. Aqueous slips are dangerous even when surfactants are used because water can exhibit activity during drying due to the high surface tension and cause aggregation and nonequidensity. Slips in organic liquids using pressure casting are more promising. However, such media make it difficult to obtain sedimentation and aggregately stable slips and create problems in environmental protection and fire safety.

Firing, where growth of crystals beyond the nanosize limits is possible, is the most complicated stage in production of nanoceramics. Hot molding, hot isostatic molding, super fast sintering, and combinations of the above are promising for preserving the nanosize of the crystals in ceramics. In super fast sintering, small semiproducts can be placed in and rapidly removed from the heated furnace after sintering ends so that the crystals cannot grow beyond nanosized. It is more promising to use high-frequency (microwave) heating, which allows rapidly and, especially important, uniformly heating the semiproduct. Crystals begin to grow intensively after the infinite cluster of open pores disappears (this is usually approximately 10 – 15% of open pores) [4]. If such porosity is acceptable, keeping the crystals nanosized is significantly facilitated. Ceramics and ceramic composite materials are manufactured with the initial nanopowders.

Manufacture of nanoceramics consisting of nanocrystals is very complicated, although all stages are the same as in traditional ceramics, only using nanoparticles. Special attention should be focused on preventing the nanoparticles from reacting with the environment, i.e., it is necessary to store powders, molding paste, molded semiproducts, and porous ceramic items to prevent undesirable reactions with the environment. Contact with water in the liquid or gas phase is very

dangerous. Use of nonaqueous organic media is most harmful to the health and a fire hazard, and frequently also dangerously explosive.

A second way of manufacturing nanoceramic materials is more promising for rapid implementation. There are now two methods of implementing it. The first method of implementing the second way consists of direct production of nanoparticles in the stage of heat treatment of the ceramic. Condensation and sintering of the material are conducted in a special mold using intensive deformation, for example, additional rotation of the molded mass. The initial crystals used today in ceramics technology can be broken down to nanosize. As a result, nanoceramic semiproducts are obtained and after mechanical processing, are converted into articles of the required size and shape. Hot-molding equipment, which is still expensive, that allows rotating the molded and sintered semiproduct is required for implementing the method. Fabrication of large sintered semiproducts is problematic. It is necessary to have specialists and equipment for mechanical processing of nanoceramics. For this reason, this method, despite its simplicity, is still complicated for industrial realization.

The second method is most promising. It utilizes solid-phase systems — unstable solid solutions, chemical compounds, and polymorphous phases which begin to decompose on heat treatment in the solid state with separation of a nanosized phase that determines the performance properties of the material and which are rightfully nanocomposites. The possibility of keeping the separated phases nanosized is facilitated by the relatively slow occurrence of diffusion mass transfer in the solid phase. This allows inhibiting the process after attaining the required nanosize.

In this case, the size of the other crystals will be much larger than the particles in the nanosized phase, and all process stages will almost not differ from the traditional stages except for the firing conditions, which must ensure formation of nanoparticles. The process of obtaining the nanosized phase can be combined with sintering or can be a special stage. The temperature conditions of firing must be regulated so that the unstable phase is separated and not allowed to increase beyond nanosized limits.

The search for unstable solid-phase systems is the main restriction in this method. There are not many of them in comparison to the possibility of mixing the most varied components in traditional ceramics technology. In this method, traditional equipment and process methods can be used except for the firing or additional heat treatment regimes. When the unstable systems and firing regimes have been selected, this method can be relatively easily implemented in traditional ceramics plants.

Adding nanoparticles in the amount of 2–5%² to traditional ceramic pastes is very promising. If the chemical composition of the nanoparticles and traditional ceramic paste and the firing conditions can be selected so that the nano-

particles retain the required chemical composition, do not go beyond the limits of nanosize, and the most important performance property of the material is determined, then it will be a nanoceramic, more precisely, a nanocomposite, with an ordinary ceramic matrix. The fundamental problem will be selecting the appropriate composition and the uniform distribution of the small number of nanoparticles in powder in which the particles are tens and hundreds of times larger. The parameters of the remaining process operations are close to the traditional parameters.

Nanoparticles are promising for use as modifying additives to reduce the sintering temperature and increase the quality of the products. Nanoparticles can be used not only as products but also as precursors, metals, for example, which turn into oxides on firing in oxidizing medium. As stated previously, nanoparticles have a lower melting point and the atoms in them begin to participate in mass transfer processes in sintering of the ceramic at lower temperatures due to the weakened chemical bonds. The decrease in the firing temperature obtained and the increase in the quality of the ceramic articles can be totally advantageous economically. Although the nanoparticles disappear, this process belongs to nanotechnologies since the number is controlled and the presence of nanoparticles has a positive effect. The changes in the process limit parameters will be small except for the uniform distribution of 2–5% of the nanoparticles over the surface of larger particles. The enterprise will gradually begin to acquire experience in working with nanopowders.

Template methods are very promising for manufacturing ceramic nanomaterials and nanocomposites. Objects that ensure obtaining material of the required shape and size are called templates. Template methods are divided into negative (Fig. 3), where the new phase fills cavities, and positive (Fig. 4), where the new phase is formed around the template. Such template methods are widely used in traditional ceramics technology. The mold for casting of ceramic slip is a negative template, while the cold metal part in which hot wax slip is frozen in production of ceramic crucible semiproducts is a positive template.

Zeolites are an example of natural negative templates with nanopores. Thermal decomposition of organosilicon polymers is used, for example, for creating nanoporous ceramics from SiO₂ [5]. The size of the nanopores can be regulated by changing the size of the functional groups in the polymer removed on degradation. The method is a reproduction on the nanolevel of the well-known method of manufacturing porous ceramics using additives that burn out. To create pores in ceramics, sawdust or coke is added to the molding paste and form pores when they burn off during firing.

A nanosized negative template can be obtained in selective etching of complex oxides or an eutectic with nanoparticles. For example, the MnO nanoporous ceramic was fabricated by removing ZnO from a dense ceramic consisting of ZnMn₂O₄ in reducing conditions in passing a mixture of 5% hydrogen in nitrogen [6]. In reducing conditions, Mn₂O₃ turns into MnO with a decrease in the volume. A MnO nano-

² Here and below — content by weight if not otherwise indicated.

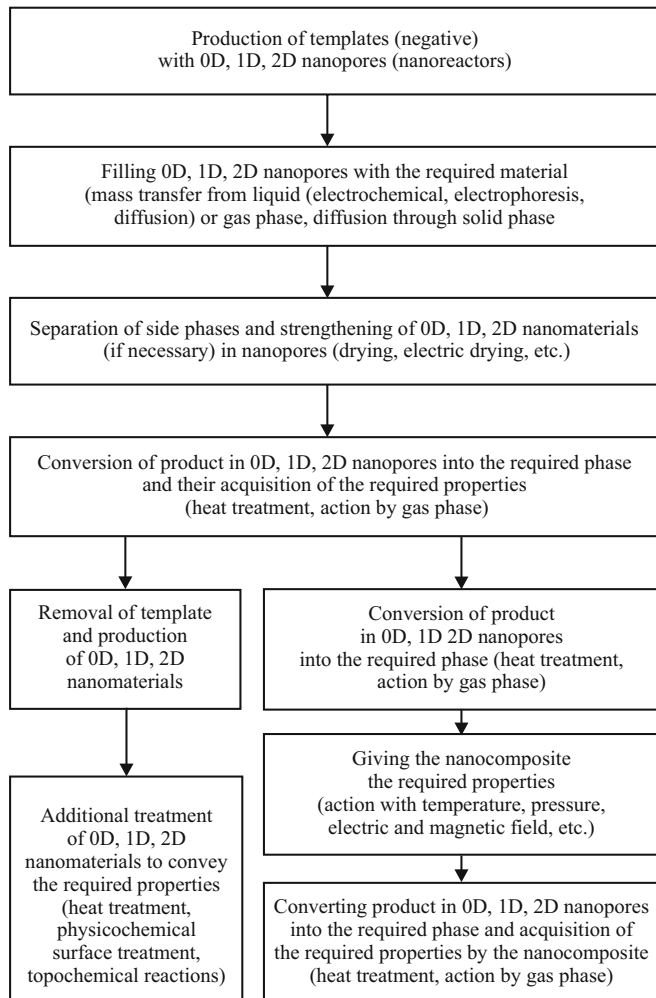


Fig. 3. Diagram of production of 0D, 1D, and 2D nanomaterials and nanocomposites with a disperse phase of 0D, 1D, or 2D nanomaterials using negative templates.

porous ceramic with an average open passable nanopore size of 50 – 200 nm was obtained as a result. The nanopores had faceting and were mutually oriented perpendicularly, the consequence of inheriting elements of the structure of ZnMn_2O_4 in topochemical reactions of removal of ZnO and reduction of Mn_2O_3 into MnO. This ceramic is promising for sensors and catalysts and nanocomposites after the pores (negative template) are filled with another substance.

The nanopores in the template can be filled with the required material using mass transfer in the liquid phase. It is expedient to use electrochemical precipitation of metals, electrophoresis of nanoparticles, filling with melt, and diffusion of components with their precipitation in the nanopores. The nanopores can be filled in the gas phase by physical or chemical precipitation. The pores can also be filled by solid-phase diffusion over the surface of the pores or over crystal boundaries. By conducting synthesis of precursor in nanopores, the material can be compacted if necessary due to the increase in the volume in chemical reactions in a nanoreac-

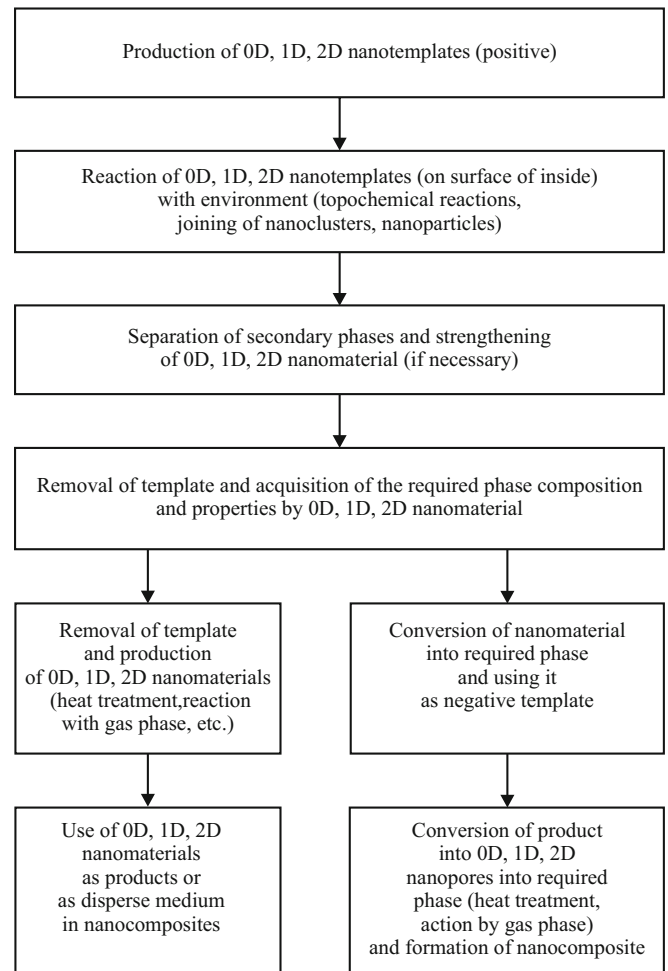


Fig. 4. Diagram of production of 0D, 1D, 2D nanomaterials and nanocomposites with disperse phase of 0D, 1D, 2D nanomaterials using positive nanotemplates.

tor. For example, in oxidation of the metal filling the nanopores, its volume can increase. In some cases, the semi-product can be compacted after filling of the nanopores by cold molding and subsequent heat treatment to heal the defects that appear or by hot (hot isostatic) molding.

We can cite the use of molecules of deoxyribonucleic acid (DNA), which has the form of a double helix with nanodimensions (except for some viruses containing single-chain DNA) and serves for transmitting genetic information in nature, for fabrication of 1D nanomaterials as an example of positive templates. An important feature of the DNA molecule is its ability to localize ions, molecules of their associate, and nanoparticles from elsewhere in its functional groups. This makes it possible to obtain a relatively wide assortment of nanomaterials from 5 nm to several micrometers in size from different substances in implementing the principle of self-organization widely used in nature and in supramolecular chemistry. A method has been developed for straightening and orienting DNA molecules on the surface of silicate glass [7]. A drop of water moved by a gas stream

leaves behind stretched and oriented DNA molecules. Further chemical and heat treatment allows fabricating nanowires from the ceramic.

Template methods are promising but require the use of ceramics technology far from the traditional technology. Other specialists and other equipment than those available in traditional ceramics plants are required for implementing these methods. Obtaining nanosized templates (positive or negative) is an important problem. Filling nanoreactors with the required phase, drying it, and converting it into the required compound are complex problems.

The technology for ceramic nanomaterials made of nanopowders has its own characteristics related to the properties of the nanoparticles and the necessity of preserving the structural elements that determine the basic performance property of the material within the limits of nanodimensions.

It is useful to begin assimilation of nanotechnologies with an evaluation of the economic effectiveness of utilizing nanopowder additives in existing ceramic pastes, especially in the form of modifying additives. If this is economically justifiable, its introduction should not significantly alter the ceramic conversions except for the uniform distribution of nanoparticles over the surface of the larger particles in the traditional paste. Another promising method of integrating nanotechnologies is production of nanoceramics from powders with a particle size much larger than nanosize and nanostructures are created during heat treatment in decomposition of unstable solid phases. All stages of ceramics technology, except for firing regimes, do not differ from the traditional stages. Selecting systems with unstable solid phases promising for use is the basic problem.

When a hot molding mold with the possibility of deformation of the molded semiproduct is used, traditional powders can be utilized and destroyed during sintering to nanosize. An addition problem is that the nanomaterial semiproduct obtained must be mechanically processed to

fabricate the article. Making nanoceramics from nanopowders is the most complicated. Although all stages of manufacturing the ceramic are the same as for ceramics with larger initial powders, all parameters of these stages can change significantly due to the characteristics of the properties of the nanopowders.

Using negative and positive templates is an effective method of creating nanocomposites, but their fabrication is a complex problem. Filling the cavities in the negative templates with precursor and converting it into product, and also filling the composite are problems. This makes it necessary to use special equipment and special process methods which are not typical of ceramics plants.

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